Discharge of Herbicides From the Mississippi River Basin to the Gulf of Mexico, 1991–97

Introduction

Current (1998) agricultural practices in the United States rely extensively on pesticides for crop production. Of the more than 500 million kilograms (kg) of pesticides used annually in the United States to control weeds, insects, nematodes, and other pests, about 20 percent are herbicides applied to field crops in the Mississippi River Basin (fig. 1). Because many herbicides are relatively water soluble and mobile, they can be transported in surface runoff from agricultural fields to streams. Although herbicides have many benefits, they may also produce toxic side effects that may pose a potential hazard to human health and the environment. For instance, the U.S. Environmental Protection Agency classifies the herbicide alachlor as a human carcinogen, and several other herbicides including atrazine, cyanazine, and metolachlor are classified as possible human carcinogens. In addition, the effects of long-term, low-level concentrations of herbicides or combinations of herbicides on aquatic ecosystems are largely unknown.

Studies conducted by the U.S. Geological Survey (USGS) have documented the presence of herbicides in the Mississippi River and its tributaries. These studies have found that concentrations of herbicides are largest for several weeks to several months following their application to farmlands. In some small watersheds in the Mississippi River Basin, concentrations of herbicides in streams have been found to exceed 50 µg/L (micrograms per liter) for short periods of time following spring storms. Discharge from small streams transports herbicides into large rivers such as the Mississippi, Missouri, and Ohio. Although herbicide concentrations in large rivers are generally not as high as in many small streams, the cumulative mass of herbicides, which eventually discharge to the Gulf of Mexico, can be large.

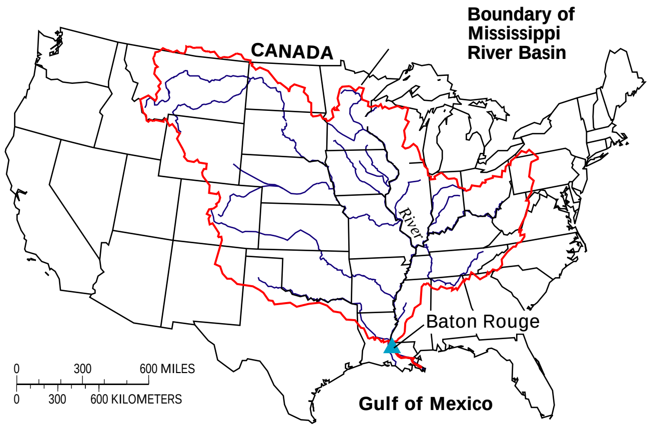

Figure 1. Boundary of Mississippi River Basin and location of sampling site.

During 1991–97 use of five herbicides (acetochlor, alachlor, atrazine, cyanazine, and metolachlor) on corn and soybeans accounted, on average, for about 70 percent of the annual herbicide use on field crops in the Mississippi River Basin (U.S Department of Agriculture, 1992–97). However, some changes in the quantity and relative use of these herbicides occurred over that time period. In 1997, total use of acetochlor, alachlor, atrazine, cyanazine, and metolachlor was about 65,000 metric tons, a decrease of about 12,500 metric tons from the amount used in 1991. Although use of atrazine and metolachlor remained relatively stable during 1991–97, alachlor use decreased by about 19,000 metric tons or 85 percent, and cyanazine use decreased by about 3,100 metric tons or 30 percent. The introduction and use of the corn herbicide acetochlor in the United States in 1994 partially offset the decrease in alachlor and cyanazine use, and by 1996 acetochlor was the third most extensively applied herbicide on corn in the Midwestern United States.

To better understand the occurrence, temporal variability, and load of herbicides in the Mississippi River, the USGS collected herbicide data from the Mississippi River at Baton Rouge, Louisiana (fig.1), during 1991–97. A total of 271 samples were collected and analyzed for 12 herbicides and 4 metabolites or breakdown products (table 1). These herbicides represent the majority of herbicide usage in the Mississippi River Basin and are the ones most frequently detected in streams. Samples were collected between 17 and 60 times per year. Herbicides were removed from water samples by extraction with organic-phase (C-18) cartridges. Samples were analyzed in the laboratory by either gas chromatography/mass spectrometry or immunoassay. The analytical reporting limit for individual herbicides was 0.05 to 0.2 µg/L.

Herbicide Occurrence in the Mississippi River at Baton Rouge

The total herbicide concentration (sum of the herbicides listed in table 1) in the Mississippi River at Baton Rouge during 1991–97 varied seasonally with the largest concentrations occurring during May through August (fig. 2). This seasonal pattern has been noted in many streams in the Mississippi River Basin and has been termed the "spring flush." Although individual herbicide concentrations in some Mississippi River Basin streams have been reported to exceed 50 µg/L, total herbicide concentrations in the Mississippi River at Baton Rouge did not exceed 10 µg/L during 1991–97 (fig. 2). Smaller, more drawn-out herbicide peaks in the Mississippi River, compared with peaks in smaller streams, are attributable to the

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Table 1. Herbicides and herbicide metabolites analyzed in samples from the Mississippi River at Baton Rouge, Louisiana, 1991–97

[µg/L, micrograms per liter]

Herbicide or metabolite	Type of herbicide	Number of samples	Years sampled	Analytical reporting limit (µg/L)
Acetochlor	acetanilide	120	1994–97	0.05
Alachlor	do.	271	1991–97	.05
Alachlor ESA	metabolite	160	1993–97	.10
Ametryn	triazine	198	1991–97	.05
Atrazine	do.	271	1991–97	.05
Cyanazine	do.	245	1991–97	0.05–0.20
Cyanazine amide	metabolite	88	1994–97	.05
Deethylatrazine	do.	245	1991–97	.05
Deisopropylatrazine	do.	245	1991–97	.05
Metolachlor	acetanilide	271	1991–97	.05
Metribuzin	triazine	243	1991–97	.05
Prometon	do.	199	1991–97	.05
Prometryn	do.	199	1991–97	.05
Propazine	do.	199	1991–97	.05
Simazine	do.	271	1991–97	.05
Terbutryn	do.	115	1993–97	.05

integrating effect of the Mississippi River, which receives input from many smaller streams. These smaller streams may drain areas of variable land use and crop groups and may deliver herbicides to the Mississippi River at different times during the growing season. Peak herbicide concentrations at Baton Rouge also may be attenuated by the presence of upstream reservoirs, which collect and store the spring flush of herbicides, subsequently delivering smaller concentrations downstream for longer periods of time (Goolsby and others, 1993).

Of the seven most frequently detected compounds in the Mississippi River at Baton Rouge, four were breakdown products, or metabolites, of herbicides (fig. 3). Individual herbicides and metabolites detected in more than 50 percent of the samples were alachlor ESA, atrazine, metolachlor, deethylatrazine, and cyanazine. In general, concentrations of these five herbicides and metabolites also were higher than concentrations of the other herbicides analyzed (fig. 3). No herbicide or metabolite was detected at a concentration exceeding 5 µg/L.

Concentrations of atrazine, cyanazine, and metolachlor in the Mississippi River generally peaked simultaneously in late May and early June, then decreased to preplant levels by the end of August (fig. 4). Acetochlor was first detected in the Mississippi River at Baton Rouge in 1995 (fig. 4), 1 year after its initial introduction for use in the United States. Coincident with the increase in the number of detections of acetochlor starting in 1995 was a decrease in concentrations and the number of detections of alachlor. However, the alachlor metabolite alachlor ESA was detected in most of the samples collected during the growing season during 1995–97. Alachlor ESA is less toxic than the parent compound but is more persistent, has a greater mobility in soil and water, and is more frequently detected in ground water throughout the Midwest.

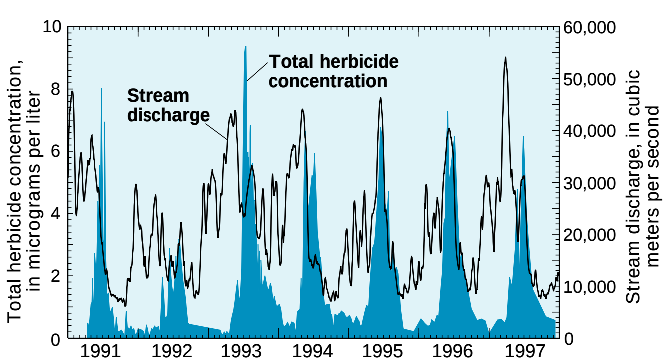

Figure 2. Stream discharge and total herbicide concentration in the Mississippi River at Baton Rouge, Louisiana, 1991–97. The total herbicide concentration represents the sum of the herbicides and metabolites listed in table 1.

Maximum Contaminant Levels (MCLs) and Health Advisories (HAs) for pesticide concentrations in drinking water have been established for a number of herbicides by the U.S. Environmental Protection Agency. Whereas MCLs are legally enforceable drinking-water regulations, HAs are drinking-water criteria and nonenforceable. The concentration of atrazine exceeded the MCL of 3 µg/L in 11 of 271 samples (fewer than 5 percent). Cyanazine concentrations exceeded the HA of 1 µg/L in 15 of 245 samples (6 percent). Alachlor and simazine concentrations did not exceed their MCLs of 2 and 4 µg/L, respectively. However, because MCLs and HAs are based on annual average concentrations, one or more exceedances of the specified value does not necessarily indicate noncompliance. None of the average annual concentrations of the herbicides examined in this study exceeded MCLs or HAs.

Herbicide Load to the Gulf of Mexico

The load, or mass per unit time, of herbicides delivered to the Gulf of Mexico was estimated to examine trends in herbicide transport in the Mississippi River and to evaluate the amount of herbicide leaving the basin as a percentage of the amount applied. Daily loads were calculated by multiplying the daily herbicide concentration by the daily streamflow in the Mississippi River at Baton Rouge. Herbicide concentrations on nonsampling days were estimated by interpolating between concentrations measured on sampling days. Daily loads were summed to estimate a total load over a specified period of time.

From 1991 through 1997, the annual load of herbicides from the Mississippi River Basin to the Gulf of Mexico ranged from about 450 metric tons in 1992 to 1,920 metric tons in 1993 (fig. 5*A*). The load estimates indicate

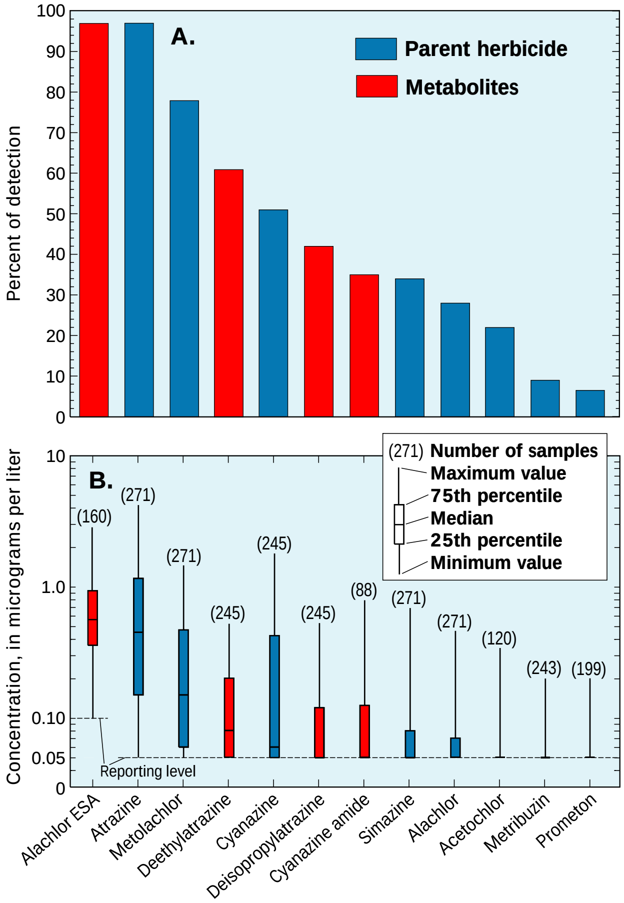

Figure 3. (A) Percent detection and (B) concentrations of herbicides and herbicide metabolites in samples from the Mississippi River at Baton Rouge, 1991–97. The herbicides ametryn, prometryn, propazine, and terbutryn were detected in less than 2 percent of samples.

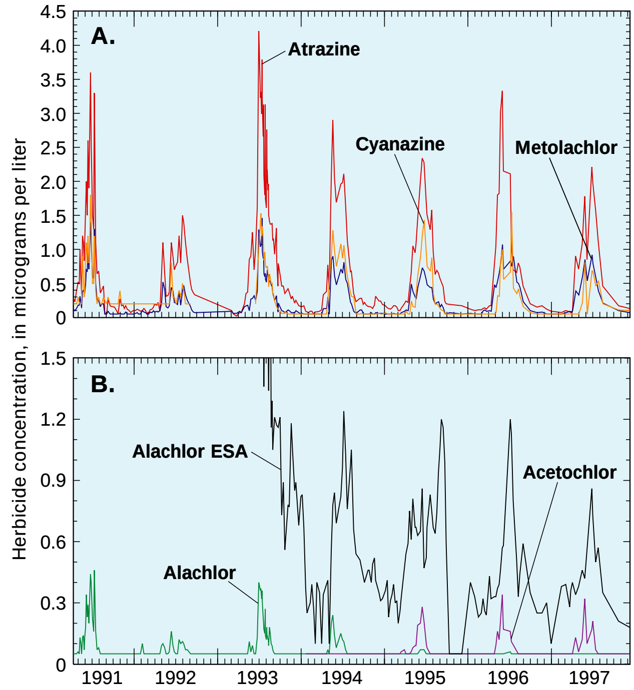

Figure 4. Temporal variation in concentrations of herbicides in samples from the Mississippi River at Baton Rouge, 1991–97.

that alachlor ESA (analyzed beginning in July 1993) and cyanazine amide (analyzed beginning in 1995) compose a large part of the annual load to the Gulf of Mexico. Nearly 80 percent of the annual herbicide load was discharged during May through August (fig. 5*B*). The largest monthly load of herbicides was discharged to the Gulf of Mexico in June when an average of about 300 metric tons, or 25 percent of the average annual total, was discharged. In June 1995, nearly 650 metric tons of herbicides were discharged to the Gulf of Mexico, the largest single monthly load of herbicides during 7 years of sampling.

Of the herbicides analyzed, atrazine composed the largest part of the load discharged to the Gulf of Mexico with a peak of about 640 metric tons in 1993 (fig. 6). This amount represented about 3 percent of the atrazine applied in the Mississippi River Basin in 1993. During 1991–97, the average annual load of atrazine represented about 2 percent of its basinwide use. If the load of atrazine metabolites (deethylatrazine and deisopropylatrazine) were included with the load of atrazine, the average annual load would represent about 3 percent of the annual basin use of atrazine. The loads of cyanazine and metolachlor in the Mississippi River were roughly equivalent during 1991–97 (fig. 6). However, during most years the amount of cyanazine applied in the Mississippi River Basin was about half that of metolachlor. Cyanazine, a triazine herbicide with properties similar to those of atrazine, is relatively mobile in the environment and is more persistent in streams than metolachlor, an acetanilide herbicide. As a result, the average annual load of cyanazine during 1991–97 was about 1.5 percent of basinwide use, and for metolachlor the average annual load was about 0.8 percent. The load of acetochlor in the Mississippi River increased from less than 3 metric tons during its first year of use in 1994 to more than 30 metric tons per year during 1995–97 (fig. 6). The load of alachlor showed a corresponding decrease from 49 metric tons in 1993 to less than 4 metric tons in 1997. The average annual load of acetochlor and alachlor, both acetanilide herbicides, represented 0.3 and 0.15 percent of the basinwide use, respectively.

The total load of acetochlor, alachlor, atrazine, cyanazine, and metolachlor as a percentage of total basinwide use varied during 1991–97 (fig. 7). The largest total use of these five herbicides occurred in 1992, when more than 81,000 metric tons were applied to crops in the Mississippi River Basin. However, the total load of these herbicides in 1992 was only about 350 metric tons, less than 0.5 percent of the use. Conversely, in 1993 the total use was about 73,000 metric tons, and the total load was about 1,200 metric tons, or about 1.6 percent of the use. Obviously, factors other than total use are important in determining the concentration and load of herbicides in the Mississippi River. Previous investigations have identified timing and method of application, spatial and temporal variations in spring storms, and annual variation in total streamflow as important factors that affect the temporal variability of herbicides in streams.

Acknowledgments

We wish to acknowledge the personnel

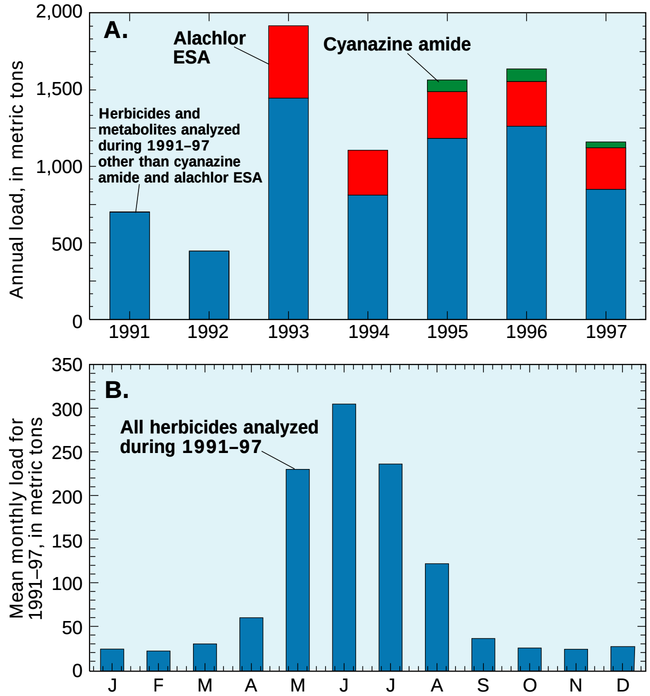

Figure 5. (A) Annual and (B) monthly loads of herbicides discharged from the Mississippi River Basin to the Gulf of Mexico, 1991–97. The 1993 load of alachlor ESA represents July–December only.

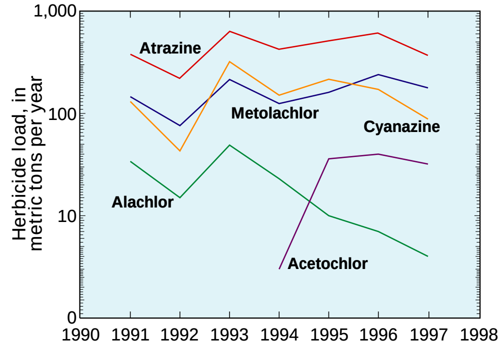

Figure 6. Annual loads of selected herbicides discharged to the Gulf of Mexico, 1991–97.

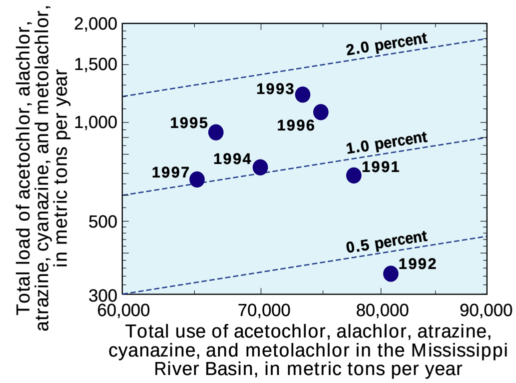

Figure 7. Relation of total annual load and use for selected herbicides discharged to the Gulf of Mexico, 1991–97. Lines are annual load as a constant percentage of annual use.

of the U.S. Geological Survey organic geochemistry laboratory in Lawrence, Kansas, for their analysis of the herbicides samples used in this publication. The analytical methods used have been described by Thurman and others (1990), and Meyer and others (1993).

—Gregory M. Clark and Donald A. Goolsby

This Fact Sheet is based on information contained in the following publication and the references contained therein:

Clark, G.M., Goolsby, D.A., and Battaglin, W.A., 1999, Seasonal and annual load of herbicides from the Mississippi River Basin to the Gulf of Mexico: Environmental Science & Technology, v. 33, no. 7, p. 981–986.

Additional References

Goolsby, D.A., Battaglin, W.A., Fallon, J.D., Aga, D.S., Kolpin, D.W., and Thurman, E.M., 1993, Persistence of herbicides in selected reservoirs in the Midwestern United States—some preliminary results, *in* Goolsby, D.A., Boyer, L.L., and Mallard, G.E., compilers, Selected papers on agricultural chemicals in water resources of the midcontin-ental United States: U.S. Geological Survey Open-File Report 93–418, p. 51–74.

Meyer, M.T., Mills, M.S., and Thurman, E.M., 1993, Automated solid-phase extraction of herbicides from water for gas chromatographic-mass spectrometric analysis: Journal of Chromatography, V. 629, p. 55–59.

Thurman, E.M., Meyer, M.T., Pomes, M.L., Perry, C.A., and Schwab, A.P., 1990, Enzyme-linked immunosorbent assay compared with gas chromatography/mass spectrometry for the determination of triazine herbicides in water: Analytical Chemistry, v. 62, p. 2043–2048.

U.S. Department of Agriculture, 1992–97, Agricultural chemical usage—1992–97 field crops summary: Washington, D.C., U.S. Department of Agriculture, National Agricultural Statistics Service, published annually.

For additional information and selected readings about the Miscontinent Herbicide Project, write to:

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Additional information on the Midcontinent Herbicide Project and other USGS programs can be found by accessing "http://wwwrcolka.cr.usgs.gov/midconherb/ind-ex.html" on the World Wide Web.

Factors for converting metric units to inch/pound units measurements:

To convert from	To	Multiply by
kilometer	mile	0.6214
kilogram	pound	2.205
ton (metric)	ton (short, 2,000 pounds)	1.102
microgram per liter	part per billion	1.0